

G2 Study of Triplet $[H_4, Si, P]^+$ Potential Energy Surface: Mechanism for Reaction of P^+ (3P) with Silane

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Received 12 February 1996; revised 25 April 1996

ABSTRACT

A G2 search of the triplet $[H_4, Si, P]^+$ potential energy surface (PES) was carried out, along with a study of a number of mechanisms for the reaction of the P^+ (3P) ion with silane. The most stable isomer, which corresponds to the species resulting from transferring three hydrogen atoms from the silicon to the phosphorus atom, lies 67.3 kcal/mol below the reactants' level. The $P^+—SiH_4$ ion–molecule complex also has remarkable stability, 20.4 kcal/mol. Bond properties were calculated and are discussed for all the stable species found on the PES. Various exothermic reaction paths were also fully characterized. The abstractions of a hydrogen molecule and a hydrogen atom, yielding species with $P—Si$ bonds, have comparable kinetic hindrance, although release of molecular hydrogen was found to be more exothermic. Finally, hydrogen and/or charge transfer reactions between P^+ (3P) and silane are also discussed. © 1997 by John Wiley & Sons, Inc.

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Introduction

Gas-phase ion-molecule reactions have recently attracted a great deal of attention because they have been recognized as one of the most likely processes to form molecules in interstellar clouds.^{1,2} This is due to the tendency of

such processes to occur via exothermic reaction pathways without energy barriers higher than the reactants' energy level, a necessary condition for a reaction to be feasible under the extreme interstellar conditions of low temperature and density. Within this context, theoretical studies on the corresponding potential energy surfaces (PESs) of ion–molecule systems are of paramount importance for the understanding of the reactivity of such ions, and for the determination of the species formed along the above-mentioned exothermic channels. These characterizations provide astrochemists with a more reliable modeling of the interstellar chemistry.

Among the second-row elements, phosphorus has attracted some interest during the last decade. Part of this interest resulted from the detection in 1987 of the first phosphorus-containing molecule in the interstellar medium, the PN species,^{3,4} and the identification of a PC molecule in the envelope of a carbon star by Guelin et al.⁵ 3 years later. Despite these detections, the suspected more abundant PO species has not been confirmed. On the other hand, several experimental studies using cyclotron resonance techniques⁶ and selected ion flow tube techniques^{7,8} (SIFT) of the reaction of P^+ and PH_n^+ with various neutral molecules pointed out their effectiveness and the propensity of phosphorus to form bonds with O, N, C, and S atoms. Also, it was claimed⁸ that the failure to detect a PO molecule could be due to total fragmentation of the atoms when the ions formed in a given ion–molecule reaction undergo electron recombination processes.

With the aim to contribute to a better understanding of ion–molecule chemistry of the P^+ ion, several theoretical works have been published on PES containing a phosphorus atom.^{9–38} Our group carried out a systematic search of the likely exothermic channels of the reactions of P^+ (3P) with several hydrides^{29–32,37,38} (CH_4 , NH_3 , OH_2 , FH , SH_2 , and ClH) and other species of interstellar interest such as C_2 , acetylene, and methanol.^{34–36} Only the reactivity of the triplet state has been studied, because it is the preferred state of the P^+ in the interstellar media. Recall that the 3P state is the ground state of P^+ , and the 1D state is the first excited state 25 kcal/mol above. Nevertheless, the 1D state has been proved to have larger bonding ability^{24–28} than the 3P state, and hence it should not be omitted when considering the overall reactivity of the P^+ cation.

In the present article we extend our previous studies to the second-row hydride SiH_4 . Silane has been detected in circumstellar shells² and is the second-row analogue of the methane, also detected in the interstellar space. In addition, inspection of the $[H_4, Si, P]^+$ PES can yield information about the behavior of the SiH_3^+ ion, whose first-row analogue CH_3^+ is crucial for the formation of several hydrocarbon containing molecules in dense interstellar clouds.^{1,2} We employed the highly accurate G2 methodology^{39–41} to determine the energetics of the various stationary points encountered on the $[H_4, Si, P]^+$ PES. Also, we comment upon the bonding features of the various minima of the PES, by means of the topological analysis of the electronic charge density and its Laplacian.⁴² Finally, Mulliken and natural population analysis (NPA)⁴³ atomic charges will also be reported.

Methods

As noted above, we used G2 methodology, with two slight modifications. Structures were optimized at the MP2/6–31G(*d*, *p*), instead of at the MP2/6–31G(*d*) level of theory. Because we deal with transition states involving H atoms, polarization functions for hydrogen, not only for heavy atoms, should be included. Frequencies were also calculated at the MP2/6–31G(*d*, *p*) instead of at the proposed HF/6–31G(*d*) level of theory. Hence, the zero point vibrational energy (ZPVE) was obtained at the MP2/6–31G(*d*, *p*) level after scaling by 0.94, as recommended.⁴⁴ Apart from these two modifications, we followed the G2 methodology closely.

All calculations were performed using the GAUSSIAN 92 suite of programs.⁴⁵ The optimized Cartesian coordinates of all the stationary points discussed in this article can be found in Table SI of the supplementary material.

G2 energies can be found in Table I. The relative stability of each minimum with respect to the reactants was calculated at the G2 level of theory and can be found in Figure 1. The reaction energy of the exothermic channels was also evaluated at the G2 level of theory and can be found in Table II.

We explored the bonding characteristics of these complexes by means of the Bader's topological analysis of $\rho(\mathbf{r})$ and $-\nabla^2\rho(\mathbf{r})$ of the MP2/6–31G(*d*, *p*) electron densities, using the AIM-PAC

TABLE I.
G2 Total Energies (hartrees), Relative Energies,
 ΔE_{G2} (kcal/mol), with Respect to
 $P^+ (^3P) + SiH_4 (^1A_1)$, and Expectation Values
 $\langle S^2 \rangle$ for Reactants, Intermediates, and
Transition States of Triplet [H₄, Si, P]⁺ PES.

Species	E_{G2}	ΔE_{G2}	$\langle S^2 \rangle$
$P^+ + SiH_4$	-631.85255	0.0	2.000
1	-631.95979	-67.3	2.006
2	-631.95900	-66.8	2.014
3	-631.95509	-64.3	2.012
4	-631.93879	-54.1	2.017
5	-631.93876	-54.1	2.021
6	-631.92374	-44.7	2.032
7	-631.91624	-40.0	2.042
8	-631.88512	-20.4	2.009
TS 2/5	-631.93608	-52.4	2.021
TS 3/7	-631.90654	-33.9	2.018
TS 1/Si	-631.90381	-32.2	2.061
TS 2/6	-631.90369	-32.1	2.029
TS 1/3	-631.90099	-30.4	2.045
TS 2/3	-631.89784	-28.4	2.051
TS 2/4	-631.89693	-27.8	2.033
TS 2/H	-631.89222	-24.9	2.010
TS 3/H	-631.87355	-13.2	2.076

series of programs.⁴⁶ Plots of the Laplacian of all the minima are depicted in Figure 2. Properties of the bond critical point (r_c), such as $\rho(r_c)$, $\nabla^2\rho(r_c)$, and the value of the energy density $H(r_c)$, for the P—Si, P—H, Si—H, and H—H bonds of all the minima are found in Table III. A bond critical point with a positive value of $\nabla^2\rho(r_c)$ can be interpreted as a point for which the electron charge is locally depleted, whereas a negative value implies that the electronic charge is locally concentrated around such point. Hence, the shape of the Laplacian can be used to characterize the nature of a bond. In this sense, if zones with negative Laplacians are linking two nuclei, we speak about shared interactions between them, as it is common to covalent bonds. On the contrary, zones with electronic charge depletion linking the nuclei are typical of ionic or van der Waals molecules and are referred to as closed shell interactions.⁴² The value of $\rho(r_c)$ can give an idea of the strength of a bond, and for a given pair of atoms can also be used as an indicator of their bond order.⁴⁷ The value of the energy density at the bond critical point can also serve to detect covalency in a bond⁴⁸ [covalent if $H(r_c) < 0$, and ionic if $H(r_c) > 0$].

Atomic charges were evaluated with the MP2/6-31G(*d*, *p*) wave function by means of the Mulliken and natural bond orbital methods. We used the GAUSSIAN 92⁴⁵ and NBO⁴⁹ programs to carry out these calculations. A complete list of calculated atomic charges is found in Table SII of the supplementary material.

Structures, Bonding, and Stabilities

Figure 1 outlines the geometry of various stable structures found on the title PES. All of them lie energetically below the reactants. We now discuss some of their salient bond and stability features, according to the following order: first isomers 5 and 8, which are formed in the entrance channel of the $P^+ (^3P) + SiH_4 (^1A_1)$ reaction; then isomers 1, 2, and 3, which correspond to the species formed through various hydrogen atom shifts from the silicon to the phosphorus atom; and finally we describe isomers 4, 6, and 7 that can be best viewed as complexes between various $[H_2, Si, P]^+$ triplet species with the hydrogen molecule.

Isomers 5 and 8 are the species formed in the entrance channel of the $P^+ (^3P) + SiH_4 (^1A_1)$ reaction, when P^+ points to one hydrogen and to the middle of two of the hydrogens of SiH_4 , respectively. Isomer 5 is interesting because the hydrogen atom in between the phosphorus and silicon is bound covalently to both of them, as revealed by inspection of its $-\nabla^2\rho(r)$ shown in Figure 2. Indeed, the analysis of the natural bond orbital gives an occupied three center bonding orbital σ_{P-H-Si} , with a population of 1.987. Nevertheless, the properties of the two bond critical points display some differences between P—H and Si—H interactions.⁴² Thus, at the P—H bond critical point, both $\nabla^2\rho(r_c)$ and $H(r_c)$ are negative (see Table III) because it is found usually for normal covalent bonds. On the other hand, at the Si—H bond critical point a decrease of the value of $\rho(r_c)$ is observed, suggestive of some degree of electrostatic type interaction. This is confirmed further by the positive value of $\nabla^2\rho(r_c) = +0.0918$, characteristic of the closed shell type of interactions.⁴² However, the energy density at bond critical point, $H(r_c)$, is -0.0258 , is suggestive of a Si—H covalent bond with a nonnegligible electrostatic contribution. Note that a similar type of bond was recently found for the ground state of the P_4H^+ species.⁵⁰

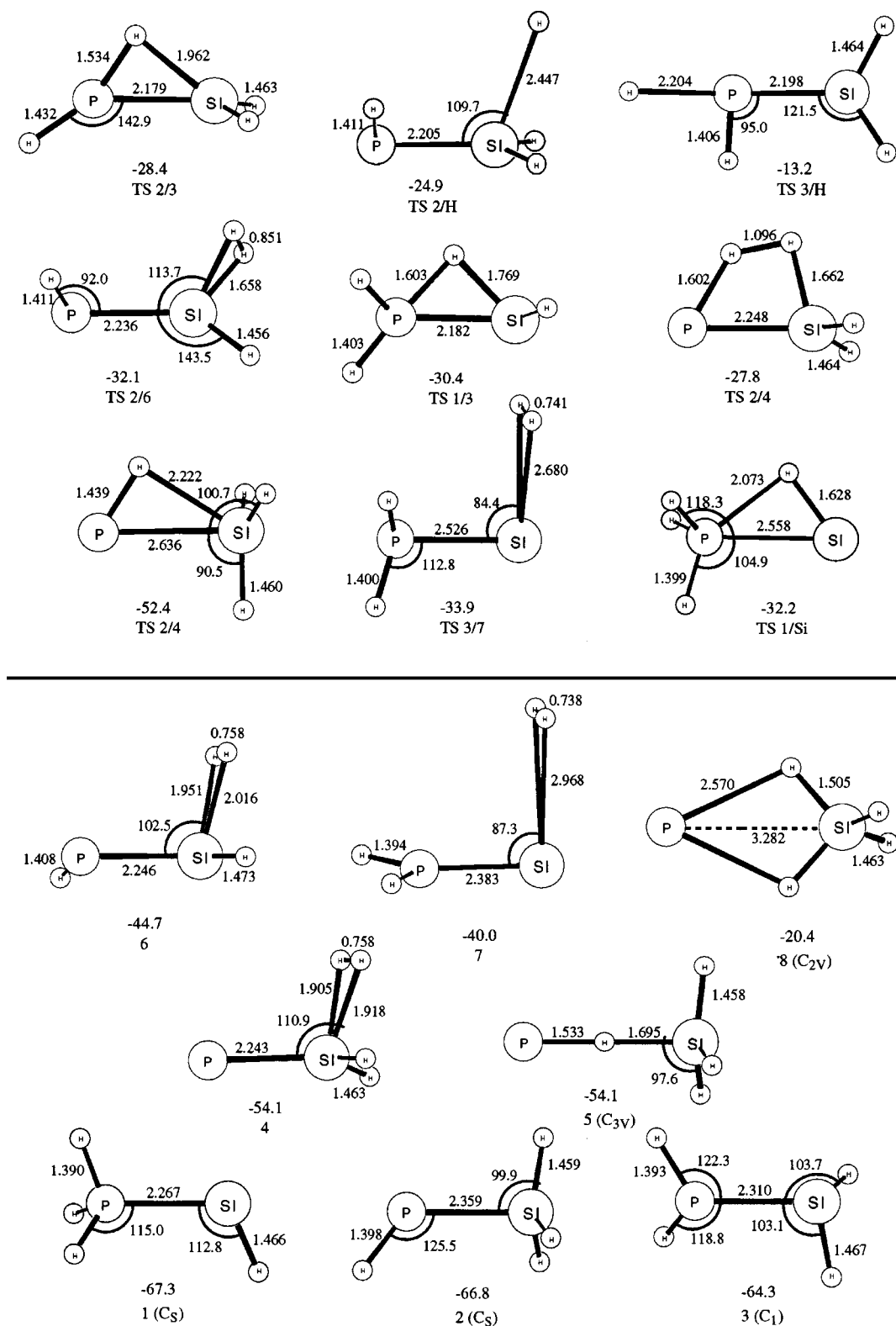


FIGURE 1. MP2/6-31G(*d*, *p*) selected geometric data and relative stabilities (G2 level, kcal/mol) of the intermediates and transition states of the triplet $[H_4, Si, P]^+$ PES. Bond lengths are in angstroms and bond angles in degrees.

TABLE II.
G2 Total Energies (hartrees) and Relative Energies (kcal/mol) for Reactants and Products of $\text{P}^+ (^3\text{P}) + \text{SiH}_4 (^1\text{A}_1)$ Reaction.

Precursors of P—Si		
Species	E_{G2}	ΔE_{G2}
$\text{P}^+ (^3\text{P}) + \text{SiH}_4 (^1\text{A}_1)$	−631.85255	0.0
$\text{PSiH}_2^+ (^3\text{A}_2) + \text{H}_2 (^1\Sigma_g^+)$	−631.93120	−49.3
$\text{HPSiH}^+ (^3\text{A}') + \text{H}_2 (^1\Sigma_g^+)$	−631.91510	−39.2
$\text{H}_2\text{PSi}^+ (^3\text{A}_2) + \text{H}_2 (^1\Sigma_g^+)$	−631.91359	−38.3
$\text{HPSiH}_2^+ (^2\text{A}'') + \text{H} (^2\text{S})$	−631.88886	−22.8
$\text{H}_3\text{PSi}^+ (^2\text{A}') + \text{H} (^2\text{S})$	−631.88750	−21.9
$\text{H}_2\text{PSiH}^+ (^2\text{A}) + \text{H} (^2\text{S})$	−631.88068	−17.6
Hydrogen and Charge Transfer Reactions		
Species	E_{G2}	ΔE_{G2}
$\text{PH}_4^+ (^1\text{A}_1) + \text{Si} (^3\text{P})$	−631.90896	−35.4
$\text{PH} (^3\Sigma^-) + \text{SiH}_3^+ (^1\text{A}_1)$	−631.90607	−33.6
$\text{PH}_2 (^2\text{B}_1) + \text{SiH}_2^+ (^2\text{A}_1)$	−631.88555	−20.7
$\text{PH}_3^+ (^2\text{A}_1) + \text{SiH} (^2\Pi)$	−631.86240	−6.2

The spin density of isomer 5 is borne by the phosphorus atom, and consequently the positive charge is largely transferred to the silicon, as revealed by the natural atomic charges, $Q_{\text{P}} = +0.628$ and $Q_{\text{Si}} = +1.207$, calculated at the MP2/6-31G(*d*, *p*) level of theory, and collected in Table SII of the supplementary material. The calculated binding energy of isomer 5 (54.1 kcal/mol) makes this entrance channel more likely than the one corresponding to isomer 8, which has a binding energy of only 20.4 kcal/mol. This intermediate 8 represents a nice example of an ion–molecule complex. Its charge is almost fully borne by the phosphorus ($Q_{\text{P}} = +0.914$), and the Laplacian of its charge density (see Fig. 2) reveals a closed shell type of interaction⁴² between the P^+ and the SiH_4 moieties. Thus the interaction of P^+ with the hydrogens of the SiH_4 are mainly of electrostatic nature, as suggested by their values of $\rho(r_c)$, $\nabla^2\rho(r_c)$, and $\text{H}(r_c)$ of 0.0147, +0.0354, and +0.0014, respectively, which are characteristic of the $\text{P}^+ \cdots \text{H}$ electrostatic type of interaction.⁵¹

Insertion of the phosphorus in the Si—H bond leads to isomer 2 of Figure 1, which is particularly stable. As shown in Table I, it lies 66.8 kcal/mol lower than the reactants at the G2 level of theory. The geometry of the molecule and the spin density, located largely on the phosphorus, can be accounted for in terms of an sp^2 hybridization of

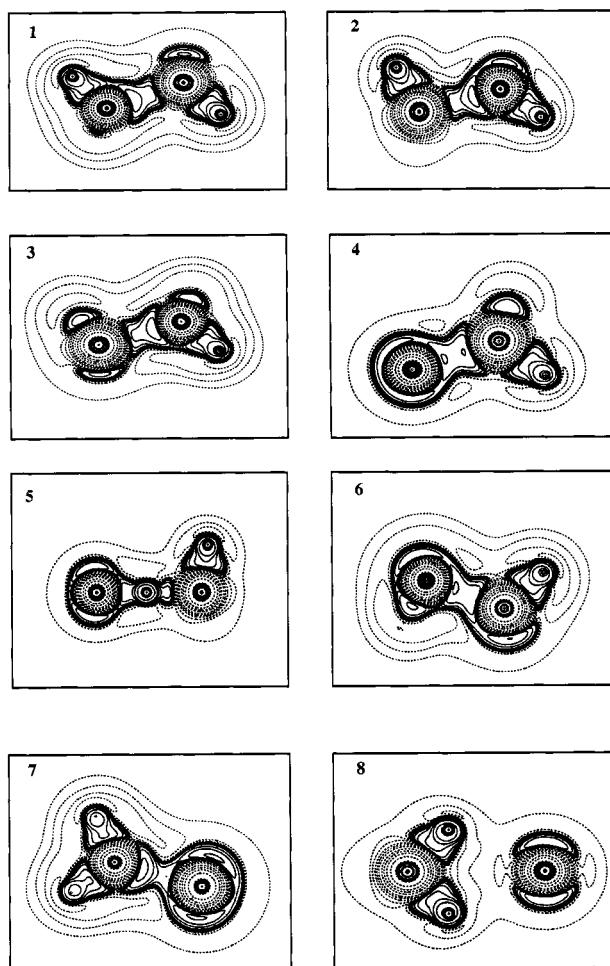


FIGURE 2. Contour maps of the Laplacian of the charge density for intermediates on the triplet $[\text{H}_4, \text{Si}, \text{P}]^+$ PES. Positive values of $\nabla^2\rho(\mathbf{r})$ are denoted by solid lines and negative values by dashed lines.

the phosphorus. The P—Si bond length of 2.359 Å and its charge density at r_c , $\rho(r_c) = 0.0642$, are suggestive of a single P—Si bond.⁴⁷

Isomer 3 is the species resulting from the migration of H from Si to P (Si, P H shift) in isomer 2. This process is found to be endothermic by 2.5 kcal/mol. Remarkably, the P—Si bond is reinforced as a consequence of the H shift; therefore, the P—Si bond length is now 0.05 Å shorter than for 2, and the $\rho(r_c)$ and $\text{H}(r_c)$ are larger and smaller, (see Table III) than for isomer 2, as expected. Si, P H shift leads from isomer 3 to isomer 1. The latter is found to be the lowest energy structure of the $[\text{H}_4, \text{Si}, \text{P}]^+$ triplet PES, 67.3 kcal/mol below $\text{P}^+ (^3\text{P}) + \text{SiH}_4 (^1\text{A}_1)$ reactants' level (see Table I). Isomer 1 has the spin density on

TABLE III.
Bonding Properties (au) at Bond Critical Point for Local Minima of Triplet [H₄, Si, P]⁺ PES.

Bond	Species							
	1	2	3	4	5	6	7	8
P—Si								
ρ	0.0850	0.0642	0.0758	0.1078		0.1009	0.0676	
$\nabla^2\rho$	0.0376	0.0125	0.0149	−0.2016		−0.1737	−0.0359	
H	−0.0537	−0.0371	−0.0468	−0.0694		−0.0687	−0.0381	
P—H								
ρ	0.1768 ^a	0.1731	0.1762		0.1109	0.1689	0.1747	0.0147
	0.1765		0.1753					
$\nabla^2\rho$	−0.0241 ^a	−0.0780	−0.0444		−0.1093	−0.0493	−0.0521	0.0354
	−0.0335		−0.0535					
H	−0.1812 ^a	−0.1779	−0.1810		−0.0903	−0.1717	−0.1792	0.0014
	−0.1813		−0.1801					
Si—H								
ρ	0.1221	0.1275 ^a	0.1250	0.1282	0.0563	0.1265	0.0064	0.1076 ^b
		0.1267	0.1240	0.0426 ^c	0.1288	0.0408 ^c		0.1239
$\nabla^2\rho$	0.2237	0.2499 ^a	0.2382	0.2338	0.0918	0.2112	0.0191	0.2367 ^b
		0.2479	0.2331	0.0746 ^c	0.2450	0.0292 ^c		0.2518 ^a
H	−0.0793	−0.0838 ^a	−0.0818	−0.0859	−0.0258	−0.0857	0.0011	−0.0636 ^b
		−0.0831	−0.0811	−0.0139 ^c	−0.0855	−0.0131 ^c		−0.0792
H—H								
ρ				0.2629		0.2612	0.2721	
$\nabla^2\rho$				−1.2834		−1.2727	−1.3918	
H				−0.3294		−0.3272	−0.3544	

^a Values for the trans hydrogen.
^b Values for the hydrogens facing P⁺.
^c Values for the interaction between H₂ and [H₂, Si, P]⁺ species.

silicon and the positive charge is borne by both the phosphorus ($Q_P = 0.305$) and the silicon ($Q_{Si} = 0.649$) atoms. In contrast to isomers **2** and **3**, isomer **1** has an sp^3 hybridization at the phosphorus, hence a shorter P—Si bond length and consequently larger $\rho(r_c)$ and smaller $H(r_c)$. The shape of its Laplacian, depicted in Figure 2, indicates a strong covalent P—Si interaction.

Isomers **4**, **6**, and **7** are best viewed as adducts of the various species of the [H₂, Si, P]⁺ system with the H₂ molecule. For each of the three species, the H₂ molecule interacts with the Si atom, given that it has the largest atomic charge. Thus, for isomer **4** the positive charge on the silicon atom is $Q_{Si} = 0.907$. The P—Si bond length of 2.243 Å is shorter than for isomers **1**, **2**, and **3**. This should be attributed to the noticeable interaction between one of the singly occupied $3p$ orbitals of the phosphorus with the empty $3p$ on Si, which has an NBO interaction energy^{43b} of 24.4 kcal/mol. This renders an enhanced charge density at the P—Si bonding region and a concomitant increase of the covalent character, reflected in the large values of

$\nabla^2\rho(r_c) = -0.2016$ and $H(r_c) = -0.0694$, as shown in Table III. The interaction of the H₂ with the Si atom for the two isomers **4** and **6** is also found to be remarkably strong and considerably weaker for isomer **7**. For instance, for isomer **4** we calculated NBO interaction energies of 51.8 and 59.2 kcal/mol for the α and β densities, respectively. In essence, they correspond with the interaction between the empty $3p$ orbital of the silicon and the doubly occupied σ orbital of the H₂ moiety. Given the large atomic charge on Si, the H₂ can get rather close, resulting in abnormally short H—Si distances for this sort of interaction.

Isomer **6** corresponds to the species resulting from the interaction of H₂ with the *trans*-[HPSiH]⁺ molecule. The atomic charge on Si is a bit larger than for **4**, namely 0.921, and the spin density is shared by the two heavy atoms. The properties of both the P—Si bond and the interaction of the Si⁺ with the H₂ moiety are very similar to those of isomer **4**. Indeed, the NBO interaction between the singly occupied $3p$ on P and the unoccupied $3p$ on Si is of 19.7 kcal/mol; for the interaction between

Si⁺ and H₂ the NBO interaction energies for the α and β densities are 37.5 and 40.2 kcal/mol, respectively. On the other hand, isomer **7** arises from the interaction of H₂PSi⁺ with the hydrogen molecule. The analysis of the natural bonding orbital reveals that the interaction between the singly occupied 3*p* on P and the unoccupied 3*p* on Si is of only 10.0 kcal/mol hence the P—Si bond length (2.383 Å) is appreciably larger than for isomers **4** and **6**. The atomic charge on Si is +0.657, a fact that results in a weaker interaction with the H₂ moiety, as evidenced by its large Si—H distance of 2.970 Å. Opposite to isomers **4** and **6**, the interaction energies between the Si⁺ and the H₂ moiety, in isomer **7**, are only 2.0 and 2.1 kcal/mol, respectively. This is suggestive of the dominance of the electrostatic effects, as illustrated in Table III. Note that the energy density at the bond critical point is positive, i.e., 0.0011, which is to be compared with its corresponding values of −0.0139 for isomer **4** and −0.0121 for isomer **6**.

In summary, apart from isomer **5**, the stable structures found on the [H₄, Si, P]⁺ triplet potential energy surface can be classified into three groups; ion–molecule complexes between P⁺ and SiH₄, isomer **8**; ion–molecule complexes between [H₂, Si, P]⁺ species and the H₂ molecule, isomers **4**, **6**, and **7**; and [H_{*n*}PSiH_{4−*n*}]⁺ species, with *n* = 1, 2, 3, isomers **2**, **3**, and **1**, respectively. For the last groups, the P—Si single bond is greatly reinforced by the interactions between the singly occupied atomic orbital of P and the empty atomic orbitals of Si.

Reaction Mechanisms

In this section we comment on the possible reaction pathway for species that could be precursors of phosphorus–silicon containing molecules in the interstellar media. We concern ourselves only with the most stable isomers of the resultant products. For all exothermic processes discussed here, at least one reaction pathway lying below the reactants' energy level was characterized, so that it can be feasible under interstellar conditions. Because the energy of the reactants cannot dissipate under interstellar conditions, reactions with all the transition states and intermediates lying below the reactants are the only ones likely.¹

The formation of isomer **5** can be considered the first step in the P⁺ (³P) + SiH₄ (¹A₁) reaction. This process is too exothermic to exhibit any transition

state, a point confirmed further by a reaction coordinate calculation at the MP2/6–31G(*d*, *p*) level of theory. The formation of **5**, 54.1 kcal/mol below the reactants' level, provides the system with an excess of energy that can be used to overcome further energy barriers through the mechanism.

The main purpose of this section is to discuss likely reaction pathways that lead to the formation of the P—Si bond. However we will also comment upon several other processes that result in the breaking of the P—Si bond. Figure 3 outlines the reaction profiles discussed later.

PRECURSORS OF P—Si

The release of H₂ from the [P—SiH₄]⁺ ion–molecule complex yields three likely precursors (HPSiH⁺, H₂PSi⁺, and PSiH₂⁺) of the P—Si molecule. We now discuss these precursors in turn. Table I presents the energies of the transition states involved in these reactions.

HPSiH⁺

Its *trans* isomer is the most stable, and it can be formed on the [H₄, Si, P]⁺ potential energy surface through the reaction pathway **I** depicted in Figure 3a. This species is obtained by dissociation of the H₂ moiety of isomer **6**. We found that this process occurs without a transition state at the MP2/6–31G(*d*, *p*) level of theory. Access to **6** from isomer **5** is possible by two consecutive steps, the former through the transition state (TS **2/5**) to reach isomer **2**; then through TS **2/6**, the complex between the HPSiH⁺ and the hydrogen molecule, isomer **6**, is obtained. The latter transition state requires substantially more activation energy than the former, 34.7 versus 1.7 kcal/mol, but it still lies well below 32.1 kcal/mol, the reactants' energy level. The whole process is found to be 39.2 kcal/mol exothermic and is therefore feasible under interstellar conditions.

H₂PSi⁺

As for HPSiH⁺, formation of H₂PSi⁺ can be achieved starting from isomer **2** (see reaction **II** in Fig. 3a) through an Si, P H shift to reach isomer **3**. The activation barrier for this step is rather high, 38.4 kcal/mol, although the corresponding transition state, TS **2/3**, remains still 28.4 kcal/mol below the reactants' energy level. Then TS **3/7** connects isomers **3** and **7**, and the latter isomer yields H₂PSi⁺ (³A₂) + H₂ (¹Σ_g⁺) without activa-

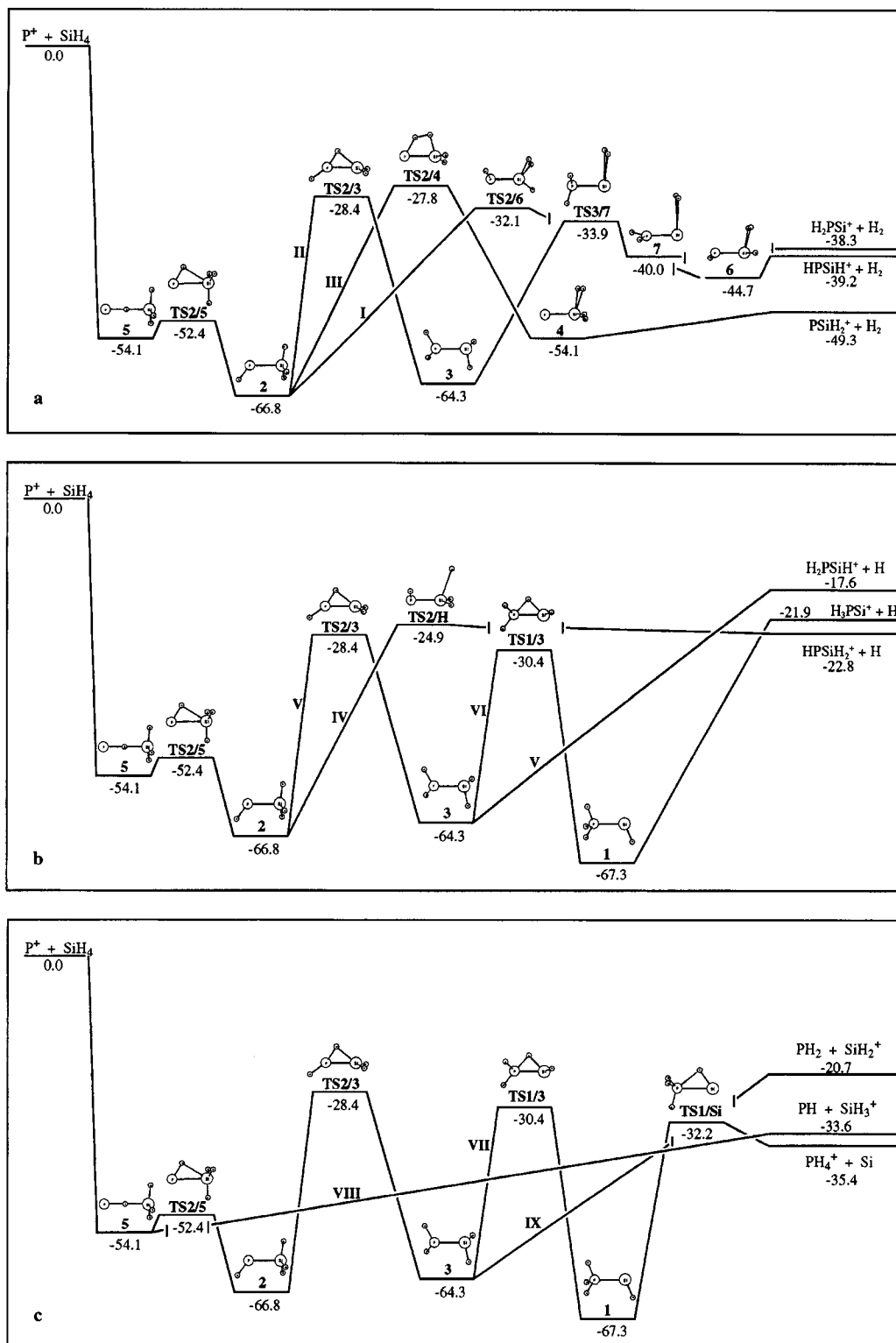


FIGURE 3. Schematic representation of the different reaction mechanisms found, calculated at the G2 level of theory (values in kcal/mol). (a) abstraction of H_2 , (b) abstraction of H, (c) hydrogen and charge transfer reactions.

tion barrier. The whole process is 38.3 kcal/mol exothermic.

PSiH₂⁺

A likely reaction for this product is pathway **III** of Figure 3a. It represents the most exothermic process found in the present study, although it has an activation barrier slightly larger than reactions **I** and **II** mentioned above. Indeed, the rate-determining step for this process is the Si, P H shift from **2**, through **TS 2/4**, which has an activation barrier of 39.0 kcal/mol, and leads to isomer **4**, which undergoes H₂ abstraction without an activation barrier to yield PSiH₂⁺ (³A₂) + H₂ (¹Σ_g⁺). The overall exothermicity of the reaction was calculated to be 49.3 kcal/mol.

It is worthwhile to indicate that there might be other mechanisms for the formation of the above-mentioned species. However, they involve abstraction of the hydrogen molecule from the phosphorus atom. Preliminary estimations of their activation energies revealed that they are more energetic than those of the reactions **I**, **II**, and **III** discussed in this section and in most cases led to transition states well above the reactants' energy level. Hence we shall not comment further on them.

The release of a hydrogen atom from the [P—SiH₄]⁺ complex produces three species, namely HPSiH₂⁺, H₂PSiH⁺, and H₃PSi⁺, that can also be considered as precursors of the PSi molecule. Likely reaction pathways for their formation have been characterized (see Fig. 3b). As shown in Figure 3b, reactions **IV**, **V**, and **VI** start out from isomer **2**, which can be obtained from isomer **5** through **TS 2/5**, as mentioned above.

HPSiH₂⁺

It is the most stable of three products discussed here, lying 22.8 kcal/mol below the reactants. It can be reached by direct hydrogen atom abstraction from isomer **2**. This process has a calculated barrier of 41.8 kcal/mol, although its corresponding transition state, **TS 2/H**, lies 24.9 kcal/mol below the reactants. Note that only neutralization of HPSiH₂⁺ (²A'') leads to a species with a singlet ground state and a P—Si double bond, hence it is difficult to synthesize and generates considerable interest even in terrestrial laboratories. In this particular case silamethylidene phosphane, HP=SiH₂, is the end result with a neutralization

energy release of 212.2 kcal/mol at the G2 level of theory.

H₂PSiH⁺

This molecular ion, which has C₁ symmetry, is the least exothermic of the three. It lies only 17.6 kcal/mol below the reactants at the G2 level of theory. It can be reached, without activation barrier, by direct hydrogen atom abstraction from the Si of isomer **3**. Access to isomer **3** is the rate-determining step for this process (see reaction **V**, Fig. 3b) with an activation energy of 38.4 kcal/mol.

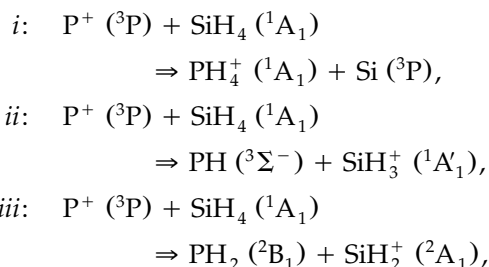
H₃PSi⁺

This species occurs with the release of 21.9 kcal/mol from the [P—SiH₄]⁺ ion-molecule complex. Like H₂PSiH⁺ it results from isomer **3**, which undergoes a Si, P H shift to give isomer **1**. This latter species yields H₃PSi⁺ without an activation barrier through the abstraction of H from the silicon atom (see reaction **VI** of Fig. 3b).

In summary, the H abstraction processes discussed in this article parallel the overall features of similar processes found for other ion-molecule complexes involving the P⁺ cation.³⁶ The mechanism involving the hydrogen shift over the less electronegative atom in the molecule and subsequent abstraction from this atom is predicted to be the most likely.

HYDROGEN AND CHARGE TRANSFER REACTIONS

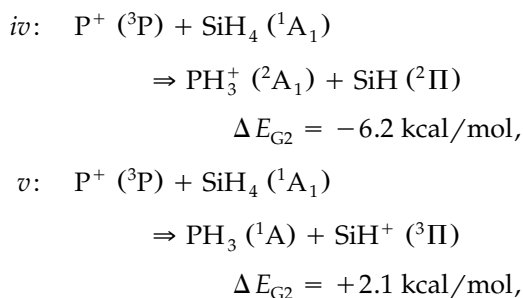
Some reactions in which only hydrogen or charge transfer or both, between fragments that contain either phosphorus or silicon, have been found to be likely competitive processes with respect to those mentioned previously which the P—Si bond is formed. Namely, we found that the following reactions can take place under the interstellar conditions:



and their mechanisms are outlined in Figure 3c. Thus, for reaction *i* a four-step mechanism was

found in which the hydrogen atoms migrate from the Si over the P one by one. All the transition states involved remain well below the reactants' energy level (see pathway VII of Fig. 3c), as well as the products, which are calculated to be 35.4 kcal/mol exothermic. The next less exothermic reaction *ii* yields $\text{PH } (^3\Sigma^-) + \text{SiH}_3^+ (^1A_1)$, and it is kinetically very favorable because it proceeds without activation barrier from isomer 5, which is the first species in the entrance channel. On the other hand, formation of $\text{PH}_2 (^2B_1) + \text{SiH}_2^+ (^2A_1)$ (see reaction IX of Fig. 3c) is achieved from isomer 3 without activation barrier through the homolitic breaking of the P—Si bond. The products are found to lie 20.7 kcal/mol below the reactants.

Finally it is worthy of mention that reactions leading to both PH_3^+ and PH_3 , namely,



have been found to be a bit exothermic and endothermic, respectively. Therefore it should not be ruled out that better calculations will not modify their relative stability order.

Concluding Remarks

The triplet potential energy surface of the $[\text{H}_4, \text{Si}, \text{P}]^+$ system was studied thoroughly. A number of stable structures, having energies lower than $\text{P}^+ (^3\text{P}) + \text{SiH}_4 (^1A_1)$, were characterized. These structures could be accessible under interstellar conditions, because the transition states of their corresponding reaction mechanisms do lie energetically below the reactants' level. In particular, it is pointed out that the formation of isomer 5 provides a significant amount of energy to overcome further energy barriers, because under the low density conditions of the interstellar media the energy cannot dissipate. The global minimum found on the triplet $[\text{H}_4, \text{Si}, \text{P}]^+$ PES is 1, a species resulting from transferring three of the hydrogens atoms of the SiH_4 to the phosphorus. Transferring less than three hydrogen atoms results in slightly

less stable compounds 2 and 3. Inspection of the bond properties for all the stable structures containing a P—Si bond reveals that the $\text{P}^+ (^3\text{P})$ has a remarkable tendency to form single bonds with silicon, contrary to the tendency shown with respect to the carbon atom,³⁶ for which partial double bonds are favored.

We also found that various adducts of the $[\text{H}_2, \text{Si}, \text{P}]^+$ species with the hydrogen molecule are remarkably stable with respect to $\text{P}^+ (^3\text{P}) + \text{SiH}_4 (^1A_1)$. In general, it was found that the H_2 molecule binds to the silicon atom by electrostatic forces, and the hydrogen atom shift process from the silicon over the phosphorus destabilizes the system.

The most likely products of the $\text{P}^+ (^3\text{P}) + \text{SiH}_4$ reaction under interstellar conditions are shown on the right side of Figure 3a–c. Note that because the low energy and temperature conditions of the interstellar space prevents energy dissipation, intermediates will be fragmented by the excess energy gained by the formation of the $\text{P}^+ \text{—SiH}_4$ ion–molecule complex. The most exothermic channels found in this work correspond to the abstraction of the H_2 molecule, which has comparable kinetic hindrance to both the abstraction of a hydrogen atom and the hydrogen and/or charge transfer from SiH_4 to the P^+ . However, for both types of reaction, a direct relation was observed between the exothermicity and the height of the barriers involved. Our study reveals, however, that formation of species containing the P—Si bond is more likely through release of molecular hydrogen than through release of atomic hydrogen. Finally, it should be mentioned that hydrogen and/or charge transfer between P^+ and SiH_4 are also likely processes. In particular, we would like to draw attention to the $\text{P}^+ (^3\text{P}) + \text{SiH}_4 (^1A_1) \Rightarrow \text{PH } (^3\Sigma^-) + \text{SiH}_3^+ (^1A_1)$ reaction that takes place with no transition state.

Acknowledgments

This research was supported by the University of the Basque Country (Euskal Herriko Unibertsitatea) and the Basque Government (Eusko Jaurlaritzak) Grant GV 203.215-0049/94, and the Basque Provincial Government of Guipuzkoa (Gipuzkoako Foru Aldundia). X. L. wishes to thank the Basque Government for a grant and E. M. C. to the Spanish A.E.C.I. for financial aid and support.

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